EFFECT OF FIBRE SURFACE TREATMENT ON KENAF FILLED RECYCLED POLYPROPYLENE COMPOSITES

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ABSTRACT

Lignocelluloses based natural fibre is being used as an alternative to traditional glass and carbon fibre in the composite materials due to its low density and higher specific properties. Furthermore, these fibres are available at a very low cost. Current work is focused on kenaf fibre based reinforced recycled polypropylene composites. In this project, initially the raw kenaf fibre was grinded to a small size (2 to 5 mm) and then mixed with recycled polypropylene (RPP) followed by extrusion through a twin screw extruder. Fibre loading in the composite was 10, 20, 30 40 and 50% by weight. After that test specimens for tensile, flexural and impact testing were prepared through an injection moulding machine. Melt flow indexer was used to evaluate the flow property of the extruded materials. To improve the interfacial property between fibre and matrix maleic anhydride grafted polypropylene (MAPP) was used as a coupling agent with ratio of 10:1. Mechanical tests showed that significant improvement achieved due to coupling agent. Fibre surface modifications for better adhesion between fibre and matrix were carried out by three ways including alkali, ultrasound and laccase enzyme treatment. Treated fibre was then blended with recycled polypropylene with 40% fibre loading in the presence of MAPP, as 40% loading found the optimum regarding tensile performances with untreated fibre based composites. For alkali treatment, both concentration of the solution and soaking time were considered as treatment variables for the fibre. Mechanical tests were carried out to evaluate the optimum treatment condition for the best strength. For ultrasound, normal water was used as media for the treatment. Both temperature and sonication power was considered as treatment variables. Mechanical tests were carried out to evaluate the best strength at optimum condition of fibre treatment. Enzymatic treatment was carried out for an alternative way of fibre treatment. The composites strength was increased by 18% for fibre loading whereas coupling agent improves it by 37%. Ultrasound and alkali treatment of fibre improved the tensile strength of the composites almost by 57%. Weathering and water uptake were carried out for the composites. After that mechanical tests were performed to evaluate the properties of the composites. Thermal test like thermogravimetric analysis (TGA) was carried out to evaluate the thermal stability of the composites. It was found that, RPP degrade at one stage while composites degrade at two stages. Activation energies of the composites were calculated from the TGA analysis. Crystallinity and melting point were detected through differential scanning calorimetry (DSC) analysis. Incorporation of fibre increased the crystallinity of the polymer matrix. Structural morphology was carried out of the fractured samples to evaluate the bonding interface between fibre and matrix. Improved adhesion between fibre and matrix was found for the case of treated fibre based composites in the presence of MAPP. Fourier transform of infrared radiation (FTIR) spectroscopy was used to find out any structural change due to the treatment of the fibre and analysis found that treatment of fibre able to remove the non-cellulosic compound to a varying extent depending on treatment parameters. Response surface method (RSM) was used to optimize process parameters and one of the best set of treatment conditions was 99.96% sonication power at 94.46 ^{o}C to achieve 28.86 MPa of TS.

ABSTRAK

Lignocelluloses berasaskan serat semula jadi yang digunakan sebagai alternatif kepada kaca tradisional dan serat karbon dalam bahan komposit kerana ketumpatan yang rendah dan sifat-sifat tertentu yang lebih tinggi. Selain itu, gentian ini didapati kos dia adalah yang sangat rendah. Kerja semasa memberi tumpuan ke atas gentian kenaf berasaskan komposit polipropilena kitar semula bertetulang. Dalam projek ini, pada mulanya serat kenaf mentah dikisar pada saiz kecil (2-5 mm) dan kemudian dicampurkan dengan polipropilena kitar semula (RPP) yang diikuti oleh penyemperitan melalui penyemperit skru kembar. Muatan Serat dalam rencam adalah 10, 20, 30, 40 dan 50% mengikut berat. Selepas itu spesimen untuk ujian tegangan, lenturan dan kesan telah disediakan melalui sebuah mesin pengacuan suntikan. Indexer mencairkan aliran telah digunakan untuk menilai harta aliran bahan tersemperit. Untuk memperbaiki harta antara muka di antara gentian dan matriks acetic maleic yang dicantumkan polipropilena (MAPP) telah digunakan sebagai agen gandingan dengan nisbah 10:1. Ujian mekanikal menunjukkan bahawa peningkatan yang ketara dicapai kerana agen gandingan. Pengubahsuaian permukaan gentian untuk lekatan yang lebih bail antara gentian dan matriks telah dijalankan oleh tiga cara termasuk ultrasound, alkali dan laccase rawatanenzim. Serat dirawat kemudian dicampur dengan polipropilena kitar semula dengan muatan gentian 40% dalam kehadiran MAPP, sebagai beban 40% mendapati prestasi tegangan optimum berhubung dengan komposit serat tidak dirawat berasaskan. Untuk rawatan alkali, kedua-dua kepekatan larutan dan masa rendaman dianggap sebagai pembolehubah rawatan bagi gentian. Ujian mekanikal yang telah dijalankan untuk menilai keadaan rawatan optimum untuk menghasilkan kekuatan terbaik. Ultrasound, air biasa telah digunakan sebagai media untuk rawatan. Kedua-dua suhu dan kuasa sonication dianggap sebagai pembolehubah rawatan. Ujian mekanikal telah dijalankan untuk menilai kekuatan yang terbaik pada keadaan optimum rawatan gentian. Rawatan enzim telah dijalankan untuk cara alternatif rawatan gentian. Kekuatan komposit telah meningkat sebanyak 18% untuk muatan serat manakala gandingan ejen meningkatkan sebanyak 37%. Ultrasound dan rawatan alkali serat meningkat kekuatan hampir 57%. Luluhawa dan pengambilan air telah dijalankan bagi komposit. Selepas itu ujian mekanikal telah dijalankan untuk menilai sifat-sifat komposit. Ujian terma seperti Termogravimetri analisis (TGA) telah dijalankan untuk menilai kestabilan terma komposit. Ia telah didapati bahawa, RPP merendahkan pada satu peringkat manakala komposit merendahkan pada dua peringkat. Tenaga pengaktifan bagi komposit dikira dari analisis TGA. penghabluran dan titik lebur dikesan melalui analisis kalori pengimbasan kebezaan (DSC). Penubuhan serat meningkatkan penghabluran komposit. Morfologi struktur telah dijalankan sampel patah untuk menilai antara muka ikatan antara gentian dan matriks. Lekatan yang lebih baik di antara gentian dan matriks telah dijumpai untuk kes kompositserat berasaskan dirawat di hadapan MAPP. Jelmaan fourier spektroskopi sinaran inframerah (FTIR) telah digunakan untuk mengetahui perubahan-perubahan struktur yang disebabkan rawatan gentian dan analisis yang dijumpai bahawa rawatan dapat serat untuk mengeluarkan kompaun bukan cellulosic ke tahap yang berbeza-beza bergantung kepada parameter rawatan. Kaedah respons permukaan (RSM) telah digunakan untuk mengoptimumkan parameter proses dan satu set keadaan rawatan yang Terbail adalah 99.96% kuasa sonication pada 94.46 ^{o}C untuk mencapai 28.86 MPa TS.

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y	Fraction of non-volatized material not yet decomposed (%)
T_{max}	Temperature at maximum reaction rate (K)
β	Heating rate (^{o}C/min)
z	Frequency factor
E_a	Activation energy (j/mol.K)
R	Gas constant ($J.K^{-1}.mol^{-1}$)
σ_t	Tensile strength (MPa)
A	Cross sectional area (m^2)
F_{max}	The maximum peak load (N)
L	Original length (mm)
L_o	Length at breaking point (mm)
E_f	Flexural modulus of elasticity (MPa)
L	Support span (mm)
m	Applied load (N)
b	Width of specimen (mm)
d	Depth of specimen (mm)
W_f	Final weight (g)
w_i	Initial weight (g)

LIST OF ABBREVIATIONS

PP	Polypropylene
RPP	Recycled polypropylene
PE	Polyethylene
LDPE	Low density polyethylene
HDPE	High density polyethylene
PVC	Polyvinylechloride
PLA	Polylactic acid
PET	Polyethylene terephthalate
MAPP	Maleic anhydride grafted polypropylene
MMC	Metallic matrix composites
CMC	Ceramic matrix composites
PMC	Polymer matrix composites
CCC	Carbon carbon composite
IMC	Intermetallic matrix composites
NaOH	Sodium Hydroxide
TS	Tensile strength
TM	Tensile modulus
FS	Flexural strength
FM	Flexural modulus
IS	Impact strength
SEM	Scanning electron microscope
FTIR	Fourier transform of infrared radiation
DSC	Differential scanning calorimetry
EDX	Energy dispersive X-ray
TGA	Thermogravimetric analysis
DTA	Differential thermal analysis
MFI	Melt flow index
WPC	Wood plastic composite
CO_2	Carbon di-oxide
PBS	Polybutadiene styrene
PS	Polystyrene
ASTM	American Society for Testing and Materials
ISO	International Organization for Standardization
HBT	1-hydroxybenzotrlazole hydrate
EDTA	Ethylenediaminetetraacetic Acid
YM	Young Modulus
RM	Malaysian Ringgit
OH	Hydroxyl group
UV	Ultra violate
MA	Maleic anhydride
KF	Kenaf fibre
TPNR	Thermoplastic Natural Rubber
EPDM	Ethylene-polypropylene-diene-monomer
RPM	Revulation per minute
RSM	Response surface methode

CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

Over the past few decades, there is a growing interest in the development of composites from natural plant fibres as a renewable source of materials. Natural fibres such as sisal, kenaf, hemp, henequen, flax, jute, oil palm empty fruit bunch, coconut fibre (coir), banana, bamboo and wood fibres are belonged to this category, and still new fibres are being added to this arena. Composites using natural fibres are on the horizon, thus bringing new trends in composite materials (Satyanarayana et al., 1990). These fibres are abundantly available in all over the world, and chemically consist of mainly cellulose, hemicelluloses and lignin. Cellulose fibres present many advantages compared to synthetic fibres, which, make them attractive as reinforcing agents in the composite materials. Although, cellulose fibres have very low strength but composites based on it posses high specific properties due to their low density. Beside this, cellulose fibres are now considered as the replacement of traditional, synthetic fibres such as glass, aramid and carbon due to their low cost, good mechanical properties, non-abrasive nature, eco-friendly and bio-degradability characteristics (Ku et al., 2011).

Although, using natural fibres in the polymer composites has many advantages, but polar fibres have low compatibility with non-polar hydrocarbon polymer matrices (examples: polypropylene and polyethylene) (Bledzki et al., 1998 and Cantero et al., 2003). Therefore, these two different categories of materials don't match properly due to their inherent nature while they are blended together for the preparation of the composites. Beside this, they can absorb moisture from the environment, due to the nature of plant based fibres; they may be attacked by the fungi which, results in low life cycle and poor interfacial bonding between fibres and matrixes etc. So, to improve the properties, initiation of the following steps has already been taken by the previous researchers. For examples, modification of the fibre surface by some chemical or enzymatic treatments, addition of coupling agent and using other additives or fillers. Nam et al. (2011) in a recent work has showed that, the mechanical properties of alkali-treated coir fibre/PBS composites are significantly higher than those of untreated fibres. The moisture absorbed by the fibres can be reduced by chemical modifications of fibres such as acetylation, mercerization (alkaline treatment), methylation, cyanoethylation, benzoylation, permanganate treatment, acrylation (Sreekala et al., 2003; Seena et al., 2005; Mishra et al., 2008; Joseph et al., 1997 and Mishra et al., 2011). The use of enzyme technology is increasing substantially in the processing of natural fibre, and the use of enzyme in the field of textile and natural fibre modification is also rapidly increasing. A major reason for using this technology is the fact that application of the enzyme is considered as environmental friendly, and the reactions catalysed are very specific with a focussed performance as a consequence. Other potential benefits of enzyme technology include cost reduction, energy and water saving, improved product quality and potential process integration (Aehle et al, 2007). Another most useful technique, which, can be introduced for fibre treatment is ultrasound treatment. This technique is already being used efficiently for physical and chemical processes due to ultrasound cavitations' effect in the liquid medium which is a growth and explosive collapse of microscopic bubbles (Liu et al., 2008). Due to sudden collapse of bubbles hot spot can be generated and localized high temperature, high pressure shock waves and severe shear force are able to break chemical bonds (Liu et al., 2008). Moreover, this process can be used as environment friendly instead of so called traditional chemical treatment of fibres using green chemistry.

Among coupling agent maleic anhydride grafted polypropylene and silane are mentionable which are using commonly to improve adhesion between natural fibres and matrices. Kim et al. (2007) in their experiment has found that, MAPP-treated composites showed strong bonding between fibre and matrix. In addition, the improved interfacial adhesion of the MAPP-treated composites was confirmed by spectral analysis of the chemical structure using attenuated total reflectance. For the case of silane, the interaction modes of the silane and matrix are dominated by the organofunctionality of silane and the matrix characteristics. Physical compatibility (such as molecular entanglement or acid–base interactions) between silane-grafted fibre and thermoplastic matrices only provides a limited improvement in the mechanical properties of the resulting composites (Xie et al., 2010).

Application and end uses determines the selection of polymers whether it would be thermoplastic or thermosetting polymer. Polyesters (Vilay et al., 2008), polyurethane (Bakare et al., 2010) and epoxy resins (Benjamin et al., 2011) among the thermosetting polymers are most commonly cited in the journals for the preparation of natural fibre based polymer composites. Among the thermoplastic polymers, polypropylene (Ichazo et al., 2001), polystyrene (Antich et al., 2006), poly vinyl chloride (Zheng et al., 2007), high density polyethylene (Mulinari et al., 2009), low density polyethylene (Sailaja, 2006), and recycled thermoplastics (Corradini et al., 2009) are commonly cited in the journals.

Polymers are petroleum based product. Petroleum is limited and will be finished in future. On the other side due to versatile use of polymer, the demand and production of it increasing sharply. This is the indication of the utilization of petroleum more than the previous time. Polymer can be reused and recycled. Thus, we should think an alternate way for the utilization of waste based plastic product to reduce the demand of petroleum. Recycling of waste based plastic can be used in making some value added products. The most developed countries like United States, Switzerland etc. are giving importance on recycling of post consumer plastics. Attempts have been made to recycle the post-consumer plastics in order to reduce the environmental impact and consumption of virgin plastics. These lead the researchers work on recycled plastic for the best use of it. Numbers of research works have been cited on recycled plastics. Interestingly, the properties of the composites made with pure plastic are same to the composites made with recycled plastic and in some cases even enhance the properties (Adhikary et al., 2008).

Natural fibre reinforced composites can be produced in many ways such as extrusion and injection molding (Suradi et al., 2010); two-roll plastic mill and hot press (YU et al., 2009), melt blending and compression molding (Lei et al., 2007). Fibres are normally processed either mechanically or chemically before mixing with polymer matrix followed by cutting into small size. After that, fibres are blended with polymer together with competibillizer (if use any) at a particular temperature for reactive processing.

The produced composites may have good strength with reasonable flexibity and can endure a moderate impact load. The interfacial adhesion may be improved due to the addition of couling agent and treatment of fibre. Combining all the properties of the composites may suit it for any application.

1.2 RESEARCH BACKGROUND

A number of natural fibres such as flax (Arbelaiz et al., 2005), wheat straw (Avella et al., 1995), pineapple leaf (Devi et al., 1997), hemp (Benjamin et al., 2011), abaca (Bledzki et al., 2010), ramie (Yu et al., 2010), coconut (coir) (Haque et al., 2009), sugarcane bagasse (Corradini et al., 2009), banana (Kazuya et al., 2004), oil palm empty fruit bunch (Khalid et al., 2008), sisal (Joseph et al., 2002), jute (Albuquerque et al., 1999), wood (kraft) (Beg et al., 2008) etc. are cited as a reinforcing agent for the composites materials with various polymer matrix such as high density polyethylene (Daniella et al., 2009), low density polyethylene (George et al., 1998), poly vinyl chloride (Zheng et al., 2007), polypropylene (Avella et al.,1995), poly styrene (Albuquerque et al., 1999), epoxy (Benjamin et al., 2011), poly lactic acid (Islam et al., 2010), poly ethylene teraphthalate (Corradini et al., 2009) etc. The various advantages of lignocellulosic plant-based fibres over synthetic fibres are low density, high specific properties, non-abrasive to the machine-equipments, non-irritation to the human skin with less health risk, low energy consumption, recyclability, renewability, low cost, and bio-degradability (Malkapuram et al., 2008). For examples, composite materials are using as parts or accessories for aerospace, building-construction, sport-item and mostly for automotive industries (Malkapuram et al., 2008; Wambua et al., 2003).

Some parameters of the composites are regardless to the selection or types of polymer matrices and natural fibres. For examples, there are many factors that can influence the performance of natural fibre reinforced polymer composites. Apart, from the hydrophilic nature of fibre, the properties of the natural fibre reinforced composites can also be influenced by fibre content or the amount of filler presence in the composite.

In general, high fibre content is required to achieve high performance of the composites. Therefore, fibre content has a significant effect on the properties of natural fibre reinforced composites.

Kenaf (Hibiscus cannabinus L)- a member of the hibiscus family, is a warm season annual fibre which is closely related to some other natural plant based fibres like jute, cotton etc. Beside that, it is biodegradable and environmentally friendly crop. In previous, it has been used as cordage crop for the preparation of twine, rope and sackcloth etc. In America, it is widely being used as a major ingredient of pulp and paper. Recently, it has been found to be an important source of fibre for composites and other industrial applications. It was found that kenaf fibre has almost 45-57% of cellulose (Bismarck et al., 2005). So, regarding the source of cellulose, it is quite good to be used in composites materials for reinforcement. Malaysian prospectus regarding kenaf production and demand are now growing faster. The renowned company, Panasonic Electric Works which is established in 2004, have monthly consumption of kenaf fibre of about 600 tonnes from a plant situated in Kuantan, Malaysia. More than 90% of kenaf fibre comes from Bangladesh, and the rest is collectively from Myanmar, Vietnam and Malaysia (Chen, 2011). Malaysian government has been given the importance on the cultivation of kenaf fibre in various states of Malaysia. Day by day, their production in all over Malaysia is increasing and the fibre quality is superior to other plant based fibre. Moreover, only after 120-150 days, it reaches near about 3-5 meter of average height. Thus, it is found to be a fast growing plant although, it is considered as a seasonal crop.

On the other hand, currently recycling rate of plastics in Malaysia is only 3 to 5% whereas; the other developed countries already achieved about 30 to 47% (Leoi, 2003). Thus, it is very much essential to increase the recycling rate of polymer based product as the resource of petroleum is limited. A variety of polymer based product such as domestic plastic goods, toys, shopping bags, containers, automobile parts such as vehicle battery case and car bumper can be recyclable when they are not useable after a long period of its life time. Moreover, a lot of other polypropylene based materials can be easily recyclable for the enhancement of the recycling rate in Malaysia.

1.3 PROSPECT OF NATURAL FIBRE COMPOSITES

About 3000 years ago, in ancient Egypt, the straw was used as a reinforcing agent in clay for the preparation of buildings. This process is even now ongoing in rural villages of almost all developing countries. After that, a long period of time natural fibre was not concerned due to the variety of innovations and attractions of others inorganic materials for their individual characteristics and applications. When the concern turn to a wide, complex and competitive market of new materials with new potentiality such as lighter weight, lower manufacturing cost, less CO_2 emission, environment friendly, easily available and most importantly when the concern come to the point that, one day our limited resources that lie in the underground will be finished, then natural fibres arise as a new research arena for a sustainable earth and it is now fast growing. In connection with that, in 1896 natural fibres and a small amount of polymer based binder were used to prepare aeroplane fuel-tanks and seats which was reported by Bledzki (1999). Composites prepared from paper or cotton, as a reinforcing agent with phenol or melamine-formaldehyde for the fabrication of sheets, pipes and tubes were reported as the first composite based materials in 1908 (Bledzki et al., 1995).

Environmental concerns drive the automakers to develop natural fibre based composites for the interior of the automobiles. Door panels, seat backs, package trays and trunk liners which were made from natural fibre based thermoplastics and thermosetting polymers (Bledzki et al., 1999). Mercedes-Benz, the famous automobile company, is using natural fibres like flax, hemp, coir and others for the interior of the vehicle body parts (Bledzki et al., 1999). Jute-coir hybrid composites for panel, flax-carbon hybrid bike, jute-PP composites for suitcase are some excellent examples of the utilization of natural fibres.

Other than that, more beneficial aspect of the utilization of natural fibre is they can be produced at lower utilization of energy and natural fibre can store CO_2 to a significant amount during their growth. Thus, both economical and environmental concern, natural fibres have a very good prospect to develop it more and more for a green world.

1.4 PROBLEM STATEMENT

- Due to versatile use, the demand of plastic and plastic made products are increasing tremendously which leads to create pressure on petroleum resources. Thus, boosting up the utilization of recycled plastic is necessary. In another way, waste based product may add some extra values to the existing product regarding cost and energy consumptions. Moreover, large amount of plastic wastage can cause serious environmental impact, also limiting land filling area whereas; in some countries this practice is totally restricted.
- Although, a number of researches have been carried out with natural fibre reinforced polymer composites, however, fibres are not compatible with most thermoplastics due to their hydrophilic nature whereas; plastics are mostly hydrophobic in nature.
- Natural fibre reinforced polymer composites also produces some problems like, easily degradable by UV radiation, high moisture absorption, low weathering stability etc.
- Chemical pretreatments or surface modifications of fibres to improve adhesion and mechanical properties of composites are drawing attention to the researchers widely. Alkaline peroxide treatment of fibre is the most common one. Still fibres reinforced composites have those problems mentioned above, and concerns of environment, health and hazard are also associated with this process. So, other methods like ultrasound, enzymatic treatment may be used to mitigate this problem. Moreover, specific properties of composites can be achieved by using those treatment processes effectively.
- There are continuous industrial pressures to invent new composite materials for sustainability which can be made from low-cost raw materials, through low manufacturing cost and low energy consumption. At the same time, environmental concerns to control green house gases emission and light- weighted natural plant based products are also their requirements.

1.5 OBJECTIVES

The major objective of this research work was the production and characterization of composites from kenaf with recycled polypropylene. More specifically the objectives are to:

- Produce composites using treated (alkali, ultrasound and enzymatic) fibres with recycled plastics and compare the mechanical properties with the untreated one.
- Investigate the effect of MAPP on the mechanical properties of the composites to enhance the interfacial bonding between fibre and matrix.
- Study the effect of extreme weathering and water uptake testing.

1.6 SCOPE

This experiment was carried out to the preparation and characterization of kenaf fibre reinforced recycled polypropylene composites. Fibre surface modification through alkali, ultrasound and enzyme were carried out, and the properties of the composites with the effect of coupling agent were studied. The scopes of this research are as follows:

1. Treatment of fibre by alkali solution with various treatment variables like NaOH concentration (3, 5 and 7%) and duration of soaking time (2, 4 and 6hrs).
2. Treatment of fibre by ultrasound with various treatment variables such as sonication power (low, medium and high) and temperature (60, 80 and 95 ^{o}C).
3. Treatment of fibre by laccase enzyme with various treatment variables like enzyme activity (60, 80 and 100 U/ml) and soaking time duration (2, 4 and 6hrs).
4. Preparation of composite with 10 to 50% fibre loading and optimization according to the best tensile strength performances.
5. Incorporation of coupling agent with a ratio of 1:10 as coupling agent to fibre.
6. Production of composites through various reactive processes such as extrusion and injection molding. Various process variables, such as temperature, screw speed and rotation were involved with this experiment. Fibre loading and fibre size

were also important considerations in this experiment. Characterizations of the composites were done by various mechanical, thermal, structural and morphological testing.